Diarylethene Modified Electrode Device. Photoswitching of the Electron Transfer of a Diarylethene with Long Alkyl Chains Embedded in a Lipid Cast Film on an Electrode

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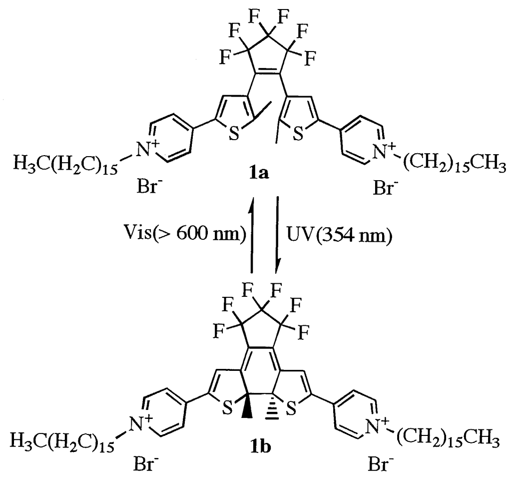
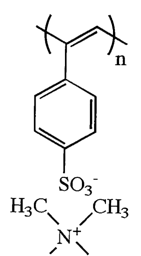
An electroactive diarylethene compound, **1** was synthesized and was embedded in a cast film of a lipid film on an electrode. This electrode device was found to possess a light-triggered optical and electrochemical switching function.

Diarylethenes with heterocyclic rings are known to possess the potential ability for many applications because of their high photofatigue resistant properties.[1-4] Very recently Lehn and coworkers reported the light-triggered redox tuning of electroactive diarylethenes dissolved in organic solvents.[3-4] We describe here, for the first time, the design and fabrication of a diarylethene-modified electrode device and its photo switching properties. An electroactive diarylethene having two long alkyl chains, **1**, was synthesized and was immobilized in a cast film of poly(ion-complexed)lipid, $2C_{18}N^+PSS^-$, on an electrode, followed by the study on the light-triggered electrochemistry of **1** on the electrode.

Compound **1** was synthesized by the reaction of 1,2-bis(2'-methyl-5'-(pyrid-4"-yl)thien-3'-yl)perfluorocyclopentene which was prepared according to the method described in the literatures[1-4] with n-hexadecylbromide in acetonitrile. The product was analyzed by the elemental analysis[5], IR, TLC and ^1H NMR.





$2C_{18}N^+PSS^-$

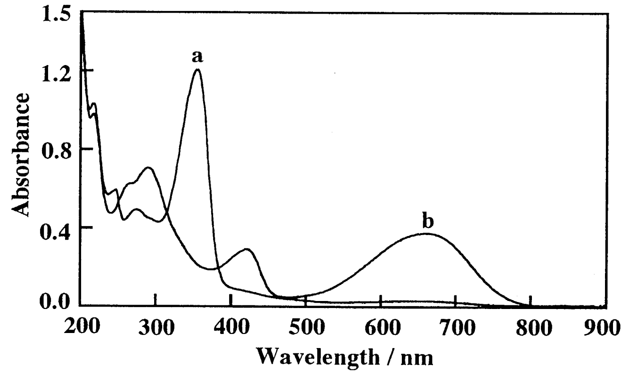


Figure 1. UV-vis spectra of compound **1** (3.0×10^{-5} mol dm^{-3} in CH_3CN) at 25 °C. (a) Visible light irradiation (30 min), (b) UV light irradiation (20 min).

Figure 1 shows UV-vis absorption spectra of **1** in acetonitrile. As is obvious from the data, UV-light irradiation causes photochemical cyclization from the open (**1a**) to closed (**1b**) forms and **1b** undergoes reversible photoisomerization *via* visible light irradiation,[6] which is typical for diarylethenes.[1-4]

Light-triggered electrochemistry of **1** was examined by cyclic voltammetry (equipment, BAS-100BW electrochemical analyzer, Bioanalytical Systems). Modified electrodes were prepared by the following procedure. A thirty microliters portion of a chloroform solution of $1\text{-}2C_{18}N^+PSS^-$ (molar ratio, 1/20 ; [**1**] = 1.0×10^{-3} mol dm^{-3}) was placed on a basal plane pyrolytic graphite (BPG) disk (geometric area, 0.25 cm^2) electrode,[7] followed by air-drying.

Cyclic voltammograms of **1** at a bare gold electrode (geometric area, 2.01mm^2) in acetonitrile is shown in Figure 2 which indicates that **1** can undergo direct electron transfer reactions with the electrode under UV-light irradiation, whereas visible light irradiation causes drastic decrease in the faradaic current. Though in our system, some electrochemical process near zero volt remains even after 30 min-visible light illumination, we could observe good photofatigue resistance on this electrochemical switching behavior, which is in accordance with the literature.[3]

Figure 3 shows cyclic voltammograms for the electrode coated with the cast film of $1\text{-}2C_{18}N^+PSS^-$ in an aqueous solution. As well the case at the bare electrode system, UV light irradiation gives well-defined redox waves attributable to the oxidation / reduction of **1b** near zero volt vs. SCE (saturated calomel reference electrode) at 55 °C which is higher than the phase transition temperature (44.7 °C)[8] of cast films of $1\text{-}2C_{18}N^+PSS^-$ (molar ratio, 1/20).[9] Visible light irradiation on the modified electrode, on the contrary, results in no

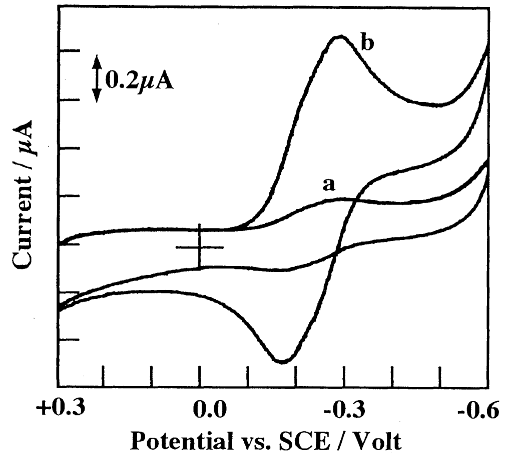


Figure 2. Cyclic voltammograms of compound **1** at a bare gold electrode in acetonitrile at 20 °C. [**1**] = 1.0×10^{-4} mol dm^{-3} (Supporting electrolyte, 0.1 mol dm^{-3} $Bu_4N^+ClO_4^-$; Sweep rate, 50 mV/s). (a) Visible light irradiation (30 min), (b) UV light irradiation (15 min).

electrochemical communication in the +0.4 to -0.15 V region. The observed light-triggered redox switching was reproducible, but the photofatigue resistance on this modified electrode is not satisfactorily, which may have resulted from lower redox stability in the reduced form of **1b**. The details on this phenomenon will be reported in subsequent publications. At temperatures below the phase transition, no faradaic current was observed at the modified electrode both under UV- and visible light illumination. We have described similar phase transition dependent electrochemistry for the redox active compounds embedded in the cast films of $2C_{18}N^+PSS^-$ on the electrodes.[10]

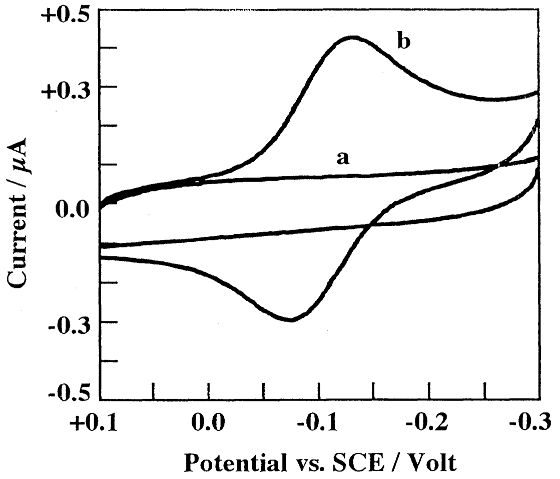


Figure 3. Cyclic voltammograms for a **1**-$2C_{18}N^+PSS^-$ (molar ratio, 1/20) cast film on a BPG electrode in an aqueous solution at 55 °C (Supporting electrolyte, 0.1 mol dm^{-3} KCl ; Sweep rate, 100 mV/s). (a) Visible light irradiation (10 min), (b) UV light irradiation (1 min).

In conclusion, we have developed a diarylethene / lipid film-modified electrode device which possesses a light-triggered optical and electrochemical switching function. Intense effort is currently under way in our laboratory to define the electrochemical characteristics of the modified electrodes and explore their potential applications toward "multimode chemical interfaces".

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References and Notes

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5 Anal. for compound **1**. Found: C, 57.85; H, 7.01; N, 2.57%. Calcd for $C_{57}H_{82}N_2S_2F_6Br_2$ · $2.5H_2O$: C, 58.10; H, 7.44; N, 2.38%.

6 The light source was a 500 W Xenon lamp (Ushio UI-501C). UV- and visible light were selected by passing the light through a visible absorbing filter (Toshiba R-60) or a UV-absorbing filter (Toshiba UV-D33S), respectively.

7 Pyrolytic graphite(Union Carbide Co.) was sheathed in an epoxy resin (Torr Seal, Barian Co.) to expose a basal-plane and connected to a glass tube. The electrode surface was polished with a 600-grit SiC paper, washed with water and then sonicated in water.

8 The phase transition temperature between crystalline phase and liquid crystalline phase for cast films of **1b**/$2C_{18}N^+PSS^-$ was determined by differential scanning calorimetry.

9 Repeated scan caused the decrease in the redox current.

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